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Troiani et al.

[11] **4,426,393**

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[54] **METHOD OF PROTECTING USEFUL PLANTS AND FORMULATIONS FOR USE IN SAID METHOD**

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Related U.S. Application Data

[62] Division of Ser. No. 98,027, Nov. 28, 1979, abandoned.

[30] **Foreign Application Priority Data**

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[52] **U.S. Cl.** **424/327**; 564/226; 564/229

[58] **Field of Search** 424/327

[56] **References Cited**

U.S. PATENT DOCUMENTS

2,947,782	8/1960	Benneville et al.	260/551
3,234,255	2/1966	Hackmann et al.	260/454

OTHER PUBLICATIONS

Bamberger et al., Berichte, vol. 35, pp. 1082–1093, 1902.

Primary Examiner—Allen J. Robinson

[57] **ABSTRACT**

There are disclosed arylhydrazo-aldoximes which, as such, as tautomers, and in the form of organic or inorganic salts thereof, are active in preventing and treating infections of useful plants by fungi, and in immunizing plants against such infections.

7 Claims, No Drawings

METHOD OF PROTECTING USEFUL PLANTS AND FORMULATIONS FOR USE IN SAID METHOD

This is a Rule 60 Division of our application Ser. No. 98,027 filed Nov. 28, 1979, and now abandoned.

THE PRIOR ART

Some arylhydrazo-aldoximes are known from the publications of E. Bemberger et al (see Berichte 35, 1902, pp. 72–74; ibid p. 1085; and ibid 36, 1903, p. 57). However, no use for such arylhydrazo-aldoximes is known except only as intermediates for obtaining other compounds.

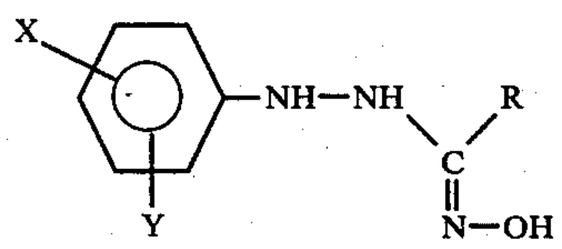
THE PRESENT INVENTION

One object of this invention is to show the biological activity of the arylhydrazo-aldoximes.

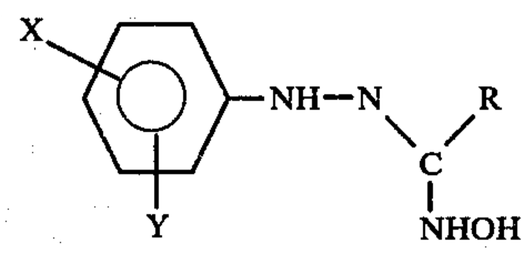
Another object is to provide a method of using arylhydrazo-aldoximes to fight infection of useful plants by fungi.

A further object is to provide new fungicidally active arylhydrazo-aldoximes.

These and other objects are achieved by the present invention based on the discovery that arylhydrazo-aldoximes having the general formula:



or their tautomers:



(I)

in which

X and Y = H, halogen, C_1–C_5 alkyl, halogenated alkyl, alkoxyl or NO_2; and

R = H, C_1–C_5 alkyl, phenyl or subsubstituted phenyl,

are active as such, or in the form of their organic or inorganic salts, and in doses of as low as 0.01%, in preventing (hindering) the infection of plants by fungi; in treating plants which have been infected; and in immunizing plants against infection by inhibiting spreading of the infection even if applied at a distance from the site of the infecting fungi.

The following Table I lists specific arylhydrazoaldoximes which we have tested and found to be fungicidally active, including arylhydrazo-aldoximes which are new products in the art as well as arylhydrazo-aldoximes known in the literature for which bibliographic data is provided in the Table. The arylhydrazo-aldoximes are prepared by methods based on the literature cited.

The arylhydrazo-aldoximes according to the present invention can be applied to the plant as such or in the form of formulates prepared by conventional techniques: they can be mixed with inert powders, such as, e.g., kieselguhr, activated carbon, gypsum, urea, etc., or they can be made to absorb, having recourse, if necessary, to surfactants, in order to obtain wettable powders; they can be also dissolved, or dispersed, or emulsified in water, or applied as solutions in organic solvents.

TABLE 1

PROPERTIES OF THE COMPOUNDS OF GENERAL FORMULA I

Item	X	Y	R	FORM (Free Base of Salt)	M.P. °C.	ELEMENTAL ANALYSIS C Calc. %	C Found %	H Calc. %	H Found %	N Calc. %	N Found %
M 9933	4-Cl	H	H	hydrochloride	118	37.87	37.60	4.00	4.01	18.93	19.00
9340	2-Me	H	CH_3		116	60.31	59.68	7.31	7.32	23.44	23.49
9341	2-Me	H	CH_3	hydrochloride	180	50.12	49.82	6.65	6.54	19.48	19.31
6980	4-Me	H	CH_3	hydrochloride	148	50.12	49.96	6.65	6.56	19.48	19.49
7048	2-Cl	H	CH_3		128	48.13	47.89	5.05	4.80	21.05	20.85
7049	2-Cl	H	CH_3	hydrochloride	185	40.70	40.63	4.70	4.62	17.80	17.46
7005	3-Cl	H	CH_3		148	48.13	48.00	5.05	5.04	21.05	21.25
7006	3-Cl	H	CH_3	hydrochloride	160	40.70	40.44	4.70	4.60	17.80	17.83
10027	2-F	H	CH_3		140	52.45	52.35	5.50	5.61	22.42	22.29
10028	2-F	H	CH_3	hydrochloride	180	43.74	43.66	5.05	5.10	19.14	19.22
7046	3-CF_3	H	CH_3		115	46.35	46.05	4.32	4.24	18.02	18.10
7047	3-CF_3	H	CH_3	hydrochloride	161	40.08	40.18	4.11	4.06	15.58	15.40
6879	4-OMe	H	CH_3		105	55.37	55.04	6.71	6.73	21.52	21.38
9390	3-Me	5-Me	CH_3		124	62.15	62.45	7.82	7.86	21.14	21.18
9391	3-Me	5-Me	CH_3	hydrochloride	170	52.29	52.37	7.02	6.89	18.29	18.15
7009	3-Cl	4-Cl	CH_3		150	41.05	41.09	3.87	3.90	17.95	18.24
7010	3-Cl	4-Cl	CH_3	hydrochloride	156	35.52	35.47	3.72	3.67	15.53	15.43
9284	3-Cl	4-Cl	CH_3	oxalate	160	38.70	39.00	3.60	3.70	15.0	15.0
9288	3-Cl	4-Cl	CH_3	p-toluene sulphonate	182	44.30	45.10	4.20	4.40	10.30	10.50
9333	3-Cl	5-Cl	CH_3		155	41.05	41.19	3,89	3.83	17.95	17.96
9335	3-Cl	5-Cl	CH_3	hydrochloride	114	35.52	35.56	3.72	3.60	15.53	15.44
9373	2-Me	H	C_2H_5		103	62.15	62.56	7.82	8.06	21.74	21.97
9374	2-Me	H	C_2H_5	hydrochloride	159	52.59	51.86	7.02	6.95	18.29	18.18
7045	4-Me	H	C_2H_5	hydrochloride	145	52.59	51.94	7.02	6.95	18.29	18.07
7087	2-Cl	H	C_2H_5		111	50.59	5.66	5.68	19.67	19.71	
7088	2-Cl	H	C_2H_5	hydrochloride	160	43.22	43.06	5.24	5.50	16.80	16.09
6984	3-Cl	H	C_2H_5		112	50.59	50.68	5.66	5.75	19.67	20.43
6985	3-Cl	H	C_2H_5	hydrochloride	148	43.22	43.03	5.24	5.23	16.80	16.97
6981	4-Cl	H	C_2H_5	hydrochloride	166	43.22	43.23	5.24	5.27	16.80	16.75
7090	3-CF_3	H	C_2H_5		106	48.58	4.89	4.73	17.00	16.93	

TABLE 1-continued

PROPERTIES OF THE COMPOUNDS OF GENERAL FORMULA 1

Item	X	Y	R	FORM (Free Base of Salt)	M.P. °C.	ELEMENTAL ANALYSIS C Calc. %	C Found %	H Calc. %	H Found %	N Calc. %	N Found %
7091	3-CF_3	H	C_2H_5	hydrochloride	155	42.34	42.53	4.62	4.57	14.81	14.86
9396	3-Me	5-Me	C_2H_5	hydrochloride	150	54.21	54.37	7.44	7.45	17.24	17.05
9466	2-Me	6-Me	C_2H_5		94	63.74	63.64	8.27	8.48	20.27	20.44
9467	2-Me	6-Me	C_2H_5	hydrochloride	145	54.21	53.51	7.44	7.50	17.24	17.02
6948	2-Me	4-Cl	C_2H_5		112	52.75	51.75	6.20	6.04	18.45	18.01
6951	2-Me	4-Cl	C_2H_5	hydrochloride	175	45.47	45.36	5.72	5.81	15.91	15.66
6882	2-Cl	4-Cl	C_2H_5		130	45.58	45.31	4.47	4.42	16.94	16.65
6982	2-Cl	4-Cl	C_2H_5	hydrochloride	182	38.00	37.91	4.25	4.26	14.76	14.62
6950	3-Cl	4-Cl	C_2H_5		125	43.57	43.06	4.47	4.40	10.93	17.11
6953	3-Cl	4-Cl	C_2H_5	hydrochloride	152	38.00	38.05	4.25	4.37	14.76	14.50
9289	3-Cl	4-Cl	C_2H_5	oxalate	147	39.70	39.59	3.87	3.96	12.43	12.25
9290	3-Cl	4-Cl	C_2H_5	p-toluene sulphonate	166	45.72	45.55	4.56	4.66	10.00	9.67
9363	3-Cl	5-Cl	C_2H_5		127	43.57	43.35	4.47	4.41	16.93	16.85
9371	3-Cl	5-Cl	C_2H_5	hydrochloride	160	38.00	37.94	4.25	4.23	14.76	14.56
7493	H	H	C_6H_4(4-Cl)	hydrochloride	148	52.37	53.13	4.39	4.84	14.09	14.07
6881	4-Cl	H	C_2H_5		98	50.59	49.65	5.66	5.60	19.67	19.36
7496	H	H	C_6H_3(3,4-Cl_2)	hydrochloride	158	46.94	46.56	3.63	3.59	12.63	12.54
6424	H	H	CH_3		Bamberger, Frei, Berichte 35, 1088						
6425	4-Me	H	CH_3		Bamberger, Berichte 35, 756						
7007	4-Cl	H	CH_3		Bamberger, Berichte 35, 59						
7008	4-Cl	H	CH_3	hydrochloride	Bamberger, Berichte 35, 59						
7043	2-Cl	4-Cl	CH_3		Bamberger, Berichte 35, 61						
7044	2-Cl	4-Cl	CH_3	hydrochloride	Bamberger, Berichte 35, 61						
6954	H	H	C_2H_5		Bamberger, Frei Berichte 35, 1092						
7495	H	H	C_6H_5	hydrochloride	Bamberger, Frei, Berichte 35, 1091						

The activity has been tested on various species of plants artifically infected with noxious fungi before (to determine the curative activity) and after (to determine the preventive activity) the treatment with the arylhydrazo-aldoxime, and by treating said plants with the fungicidal agent in parts far from the point of infection (to determine the immunizing activity).

The following examples are given for the purpose of illustrating the present invention in more detail, and are not intended to be limiting. Examples 1 and 2 illustrate the method of synthesizing the new compounds, the remaining examples concern the biological activity of some of the arylhydrazo-aldoximes within the scope of this invention.

EXAMPLE 1

M 6950

(a) An aqueous solution containing 44.5 g of 1-nitropropane and 20 g of NaOH was added, at 0° C. and in 30 minutes, to a hydro-alcoholic solution of diazonium salt prepared from 81 g of 3,4-dichloroaniline, 210 cc of concentrated HCl, 35 g of $NaNO_2$ and 225 g of trihydrated sodium acetate.

At the conclusion of the addition, the mass was stirred for 3 hours at 0° C., whereupon the resulting solid product was filtered. After washing with H_2O and drying, 125 g of 1-nitro-1-(3,4-dichlorophenylhydrazone)-propane were collected in the form of a yellow solid having a melting point of 137° C. with decomposition.

(b) 125 g of the 1-nitro-1-(3,4-dichlorophenylhydrazone)-propane were added to 400 cc of ethanol saturated at 0° C. with gaseous NH_3. Successively, anhydrous H_2S was made to bubble in the reaction mixture until evolvement of heat was no longer observed, and having ascertained that the inside temperature never exceeded 35° C. At the conclusion of the reaction, the solvent was removed at reduced pressure and the residual solid was washed with H_2O. There were obtained 75 g of β-(α-oximinopropyl)-3,4-dichlorophenylhydrazine in the form of a white solid having a melting point of 124° C. with decomposition.

EXAMPLE 2

M 6953

75 g of β-(α-oximino-propyl)-3,4-dichlorophenylhydrazine dissolved in a mixture of ethanol-ethyl ether were treated, at 5°–10° C., with anhydrous HCl up to an acid pH.

The solid which separated was filtered, so obtaining 75 g of β-(α-oximino-propyl)-3,4-dichlorophenylhydrazine hydrochloride in the form of white crystals having a melting point of 155° C. with decomposition.

EXAMPLE 3

Curative activity on vine mildew
(*Plasmopara viticola* (B et C) Berl. et de Toni)

The leaves of cv. Dolcetto vine, cultivated in pot in a conditioned ambient at 25° C. and 60% of relative humidity, were sprayed on their lower faces with an aqueous suspension of conides (200,000 conides/cc); after a residence time of 24 hours in a humidity-saturated ambient at 21° C., the plants were divided into three groups. The plants of each group were treated by spraying both faces of their leaves with the products being tested in a hydroacetone solution at 20% of acetone (vol./vol.) respectively after 1, 2 and 3 days from the infection.

At the conclusion of the incubation period (7 days), the seriousness of the infections was evaluated at sight according to indexes of an evaluation scale ranging from 100 (sound plant) to 0 (thoroughly infected plant).

Product	Dose °/oo active product	Activity
6425	1.5	75
6953	1.5	100
7007	1.5	42

-continued

Product	Dose °/oo active product	Activity
7008	1.5	100

EXAMPLE 4

Immunizing activity on vine mildew (*Plasmopara viticola* (B et C) Berl et de Toni)

The leaves of cv. Dolcetto vine, cultivated in pot in a conditioned ambient, were sprayed on their upper faces with the product being tested in a hydroacetone solution at 20% of acetone (vol./vol.).

The plants were then kept in a conditioned ambient for 6 days; on the seventh day the lower faces of their leaves were sprayed with a suspension of conides of *Plasmopara viticola* (200,000 conides/cc); after a 24-hour residence time in a humidity-saturated ambient, the plants were brought again to a conditioned ambient.

At the conclusion of the incubation period (7 days), the seriousness of the infection was evaluated at sight according to indexes of an evaluation scale ranging from 100 (sound plant) to 0 (fully infected plant).

Product	Dose °/oo active product	Activity
6425	3	100
6953	3	100
7008	3	100

EXAMPLE 5

Curative activity on the beet Cercospora (*Cercospora beticola* Sacc.)

The leaves of beet plants, cv. KWS polybeta, cultivated in a conditioned ambient, were sprayed on both faces with an aqueous suspension of conides of *Cercospora beticola* (200,000 conides/cc); after 48 hours said leaves were treated with the product being tested in a hydroacetone solution at 20% of acetone (vol./vol.) by spraying of both faces.

At the end of the incubation period (20 days), the seriousness of the infection was evaluated at sight according to indexes of an evaluation scale ranging from 100 (sound plant) to 0 (fully infected plant).

Product	Dose °/oo active product	Activity
6953	1	85
7007	1	46
7008	1	62
7010	1	100

EXAMPLE 6

Immunizing activity on beet Cercospora (*Cercospora beticola* Sacc.)

The beet leaves, cv. KWS polybeta, cultivated in pot in a conditioned ambient, were sprayed on their upper faces with the product being tested in a hydroacetone solution at 20% of acetone (vol./vol.). The plants were then kept in a conditioned ambient for 6 days; on the 7th day the lower faces of the leaves were sprayed with a suspension of conides of *Cercospora beticola* (200,000 conides/cc). After a residence time of 48 hours in a humidity-saturated ambient, the plants were brought again into a conditioned ambient.

At the conclusion of the incubation period (20 days), the seriousness of the infection was evaluated at sight according to indexes of an evaluation scale ranging from 100 (sound plant) to 0 (fully infected plant).

Product	Dose °/oo active product	Activity
6953	1	72
7007	1	86
7008	1	84
7010	1	100

EXAMPLE 7

Curative activity on cucumber oidium (*Sphaerotheca fuliginea* [Schlech] Salmon.)

The leaves of cucumber plants, cv. Marketer, cultivated in pot in a conditioned ambient, were sprayed on their upper faces with an aqueous suspension of conides of *Sphaerotheca fuliginea* (200,000 conides/cc); after 24 hours said leaves were treated with the product being tested in a hydroacetone solution at 20% of acetone (vol./vol.) by spraying of both faces.

At the conclusion of the incubation period (8 days), the seriousness of the infection was evaluated at sight according to indexes of an evaluation scale ranging from 100 (sound plant) to 0 (fully infected plant).

Product	Dose °/oo active product	Activity
6425	0.3	80
6881	0.3	80
6953	0.3	100
7007	0.3	100
7008	0.3	100
7010	0.3	87
7496	0.3	100

EXAMPLE 8

Immunizing activity on cucumber oidium (*Sphaerotheca fuliginea* [Schlech] Salmon.)

The leaves of cucumber plants, c.v. Marketer, cultivated in pot in a conditioned ambient, were sprayed on their lower faces with the product being tested in a hydroacetone solution at 20% of acetone (vol./vol.). The plants were then maintained in a conditioned ambient per 6 days; on the 7th day the upper faces of the leaves were sprayed with an aqueous suspension of conides of Sphaerotheca fuliginea (200.000 conides/cc.); then the plants were brought again into a conditioned ambient.

At the conclusion of the incubation period (8 days), the seriousness of the infection was evaluated at sight according to indexes of an evaluation scale ranging from 100 (sound plant) to 0 (fully infected plant).

Product	Dose °/oo active product	Activity
6953	0.1	100
7496	0.1	50
7008	0.1	74
7010	0.1	40

EXAMPLE 9

Curative activity on bean rust (*Uromyces appendiculatus* (Pers.) Link)

The leaves of the bean Borlotto di Vigevano, cultivated in pot in a conditioned ambient, were sprayed on their lower faces with an aqueous suspension of spores

of *Uromyces appendiculatus* (200,000 spores/cc); after a residence time of 24 hours in a humidity-saturated ambient, said leaves were treated with the product being tested in a hydroacetone solution at 20% of acetone (vol./vol.) by spraying both faces of the leaves.

At the conclusion of the incubation period (14 days), the seriousness of the infection was evaluated at sight according to indexes of an evaluation scale ranging from 100 (sound plant) to 0 (completely infected plant).

Product	Dose °/oo active product	Activity
6425	0.5	100
6881	0.5	100
7007	0.5	80
7496	0.5	100

EXAMPLE 10

Immunizing activity on bean rust
(*Uromyces appendiculatus* (Pers.) Link.)

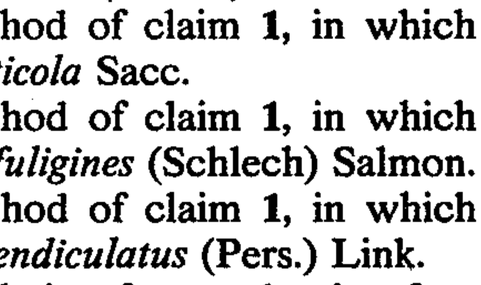
The leaves of the bean cv. Borlotto di Vigevano, cultivated in pot in a conditioned ambient, were sprayed on their upper faces with the product being tested in a hydroacetone solution at 20% of acetone (vol./vol.). The plants were then maintained in a conditioned ambient for 6 days; on the seventh day the lower faces of the leaves were sprayed with a suspension of spores of *Uromyces appendiculatus* (200,000 spores/cc); after a residence time of 24 hours in a humidity-saturated ambient, the plants were brought again into a conditioned ambient.

At the conclusion of the incubation period (14 days), the seriousness of the infection was evaluated at sight, according to indexes of an evaluation scale ranging from 100 (sound plant) to 0 (fully infected plant).

Product	Dose °/oo active product	Activity
6425	1	100
7007	1	70
6881	1	28
7496	1	95

What we claim is:

1. The method of combatting fungi infections of useful plants, or of preventing such infections, which method consists of applying to the plants a fungicidally effective amount of arylhydrazo-aldoximes having the formula:



in which

X and Y are H, halogen, C_1–C_5 alkyls, —CF_3, —OCH_3 or NO_2; and

R is H, C_1–C_5 alkyl, phenyl or phenyl substituted with 1 or 2 halogen atoms;

tautomers of said arylhydrazo-aldoximes, organic salts of said arylhydrazo-aldoximes, or inorganic salts of said arylhydrazoaldoximes.

2. The method of claim 1, in which the fungicidally active arylhydrazo-aldoxime tautomer thereof, or organic or inorganic salt thereof, is applied to the plants to be treated in an amount of at least 0.1% by weight.

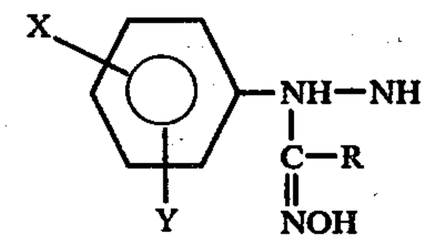
3. The method of claim 1, in which the fungus is *Plasmopara viticola* (B et C) Berl. et de Toni.

4. The method of claim 1, in which the fungus is *Cercospora beticola* Sacc.

5. The method of claim 1, in which the fungus is *Sphaerotheca fuligines* (Schlech) Salmon.

6. The method of claim 1, in which the fungus is *Uromyces appendiculatus* (Pers.) Link.

7. A formulation for combatting fungi infections of useful plants, or of preventing such infections, which formulation contain an inert carrier and, as active principle thereof, a fungicidally effective amount of arylhydrazo-aldoximes having the formula:



in which

X and Y are H, halogen, C_1–C_5 alkyls, —CF_3, —OCH_3 or NO_2; and

R is H, C_1–C_5 alkyl, phenyl, or phenyl substituted with one or two halogen atoms; tautomers of said arylhydrazo-aldoximes, organic salts of said arylhydrazo-aldoximes or inorganic salts of said arylhydrazo-aldoximes.

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